

## S P E C I F I C A T I O N

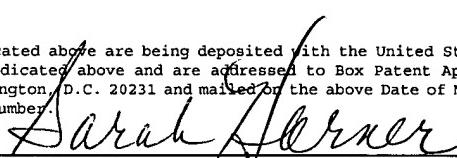
Docket No. 20480.141

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN that I, Raymond J. D'Alesandro, a citizen of the United States of America, residing in the State of Texas, have invented new and useful improvements in a

### METHOD OF REMOVING SO<sub>3</sub> FROM FLUE GASES

of which the following is a specification:

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## BACKGROUND OF THE INVENTION

1       **1. Cross Reference to Related Applications**

2       This application is a continuation-in-part of prior serial number 10/315,837, filed December 10, 2002,  
3       and entitled "Method of Removing SO<sub>3</sub> From Flue Gases", presently pending.

5       **2. Field of the Invention:**

6       The present invention relates generally to processes for treating industrial exhaust gases to remove  
7       sulfur oxides contained therein and, more specifically, to the removal of SO<sub>3</sub> from flue gases produced  
8       by combustion of carbonaceous fossil and other sulfur-bearing fuels in such industrial processes.

10      **3. Description of the Prior Art:**

11      The burning of fossil fuels and other fuels that contain sulfur, including pet coke, will result in the  
12     formation of sulfur oxides, most commonly known as SOx. The predominate species of the SOx is  
13     SO<sub>2</sub>, with minor amounts of SO<sub>3</sub>.

14

15      A variety of techniques have been developed over the years for removing SOx from facilities that  
16     burn fossil fuel such as coal burning electric generating stations as well as secondary industries  
17     operating coal burning or high sulfur oil-burning boilers. When there are high levels of sulfur that  
18     must be removed, the use of wet limestone or wet lime scrubbing are common and cost effective  
19     methods. This sulfur removal technology is based on removing the SOx from the flue gas at the end  
20     of the process. Whether the sulfur is present as either SO<sub>2</sub> or SOx is generally not of material  
21     importance, since it is the amount of total sulfur removed that is critical to the sulfur removal  
22     process.

23

24      When lower levels of sulfur are present in the fuel, typically less than 2%, then injection of dry  
25     limestone or hydrated lime into the boiler is occasionally practiced. This process tends to be less  
26     efficient and thus requires a much higher dosage of calcium reagent to sulfur removed, i.e. Ca/S >  
27     2:1 or higher.

1 Until recently there was little or no concern as to whether the sulfur removed, or the sulfur which  
2 remained in the flue gas, was either SO<sub>2</sub> or SO<sub>3</sub>, because most of the sulfur was believed to be SO<sub>2</sub>.

3

4 However, recently there has been a much greater concern regarding the presence of SO<sub>3</sub> in the flue  
5 gas, even though it is a very small amount compared to the total SOx that is emitted. With the  
6 introduction of SCR (selective catalysis reduction) in coal fired power plants to control NOx, the  
7 elimination of SO<sub>3</sub> has become a critical issue. This is partly due to the fact that an unwanted side  
8 reaction of the SCR technology to reduce NOx emissions is the catalytic reaction to form SO<sub>3</sub>. These  
9 higher concentrations of SO<sub>3</sub> are not being removed by traditional wet limestone or wet lime  
10 scrubbing systems, even if higher Ca/S ratios are used.

11

12 The higher concentrations of SO<sub>3</sub> accelerate corrosion of the air-heater, precipitator and dry gas duct  
13 components of the power plant. These pollutants are passing through all conventional sulfur removal  
14 systems and are causing high opacity plumes that contain fine droplets of sulfuric acid, H<sub>2</sub>SO<sub>4</sub>. This  
15 unexpected phenomena is causing major problems at coal fired power plants that are installing SCR  
16 systems.

17

18 A need exists, therefore, for a method for effectively removing SO<sub>3</sub> from exhaust and stack gases of  
19 fossil fired power plants.

20

21 A need also exists for a method for economically and efficiently retrofitting existing power plants,  
22 especially those that burn coal, which provides pollution reduction of SO<sub>3</sub> similar to the results  
23 achieved using wet scrubbing for SO<sub>2</sub> reduction and electrostatic precipitation for particulate removal.

24

25

## SUMMARY OF THE INVENTION

The method of the invention provides an economical and efficient means for removing SO<sub>3</sub> from off gases produced at a fossil fired power plant of the type in which utilizes a fossil fuel as a power source for the plant or in other industrial processes where sulfur containing fuels are combusted. The fuel is burned to fire the plant boilers, thereby producing off gases containing SO<sub>3</sub>. The off gases are collected in an exhaust duct which is heated by the off gases to an exhaust duct temperature.

A calcium hydroxide slurry of controlled and specified physical and chemical characteristics is injected into the off gases in the exhaust duct at a point in the duct where the exhaust duct temperature is sufficient to evaporate water from the calcium hydroxide slurry but is low enough to avoid decomposing and converting the calcium hydroxide to calcium oxide. The calcium hydroxide reacts with the SO<sub>3</sub> to produce calcium sulfate which can be removed downstream in a particulate removal station. Where SO<sub>3</sub> levels are increased in the prior art, decreased system efficiency results because of the requirement of having to set air heater exit temperatures in the plant higher, due to the increased SO<sub>3</sub> concentrations.

Preferably, the calcium hydroxide slurry is injected at a point in the duct where the exhaust duct temperature is below about 500-600EC. The calcium hydroxide slurry can conveniently be made by slaking quicklime or from lime hydrate. Preferably, the calcium hydroxide slurry is introduced into the exhaust duct through at least one nozzle with compressed air also being introduced into the nozzle to produce a plurality of lime slurry droplets, the lime slurry droplets having a particle size in the range from about 30-100 microns, dependent upon the slurry solids and air pressure utilized. The preferred solids content of the calcium hydroxide slurry so produced is in the range from about 15-35% by weight. A saturated solution of calcium hydroxide can be utilized, if desired.

In cases where the power plant has a wet scrubbing system which utilizes wet slaking of calcium oxide for the removal of oxides of sulfur in off gases, a portion of the wet slaked calcium oxide can

- 1      be diverted from the wet scrubbing system and injected into the exhaust gas duct prior to the
- 2      particulate removal system.
- 3

## **BRIEF DESCRIPTION OF THE DRAWINGS**

**Figure 1** is a simplified, schematic illustrating the principal component stations of a coal fired power plant of the type to be constructed or retrofitted to practice the method of the invention;

**Figure 2** is a simplified schematic illustrating the method of the invention=

**Figure 3** is a side, partial sectional view of a portable slaking apparatus useful in practicing the method of the invention; and

**Figure 4** is another view of the lime slaking apparatus used in the method of the invention.

1                           **DETAILED DESCRIPTION OF THE INVENTION**

2

3     The present invention relates to a simple and cost effective method for eliminating the large  
4     concentration of SO<sub>3</sub> formed by SCR systems in fossil fired power plants or if high levels of SO<sub>3</sub> are  
5     formed in such plants without SCR systems. The invention can also be utilized in other industrial  
6     processes where sulfur bearing fuels produce SOx emissions. Thus, those skilled in the art will  
7     understand that the invention is not limited to electrical generating power plants but could be applied  
8     as well to such industrial processes as cement plant kilns, expanded aggregates, etc.

9

10    Turning to Figure 1, there is shown a simplified schematic of a typical coal fired power plant. The  
11    power plant includes a primary pulverizer and air fan 11 which receives coal from a conveyer system  
12    13. The pulverizer and fan station 11 prepares the coal for burning by grinding it to a fine powder  
13    and drying and mixing it with hot air to create an efficient and combustible fuel source. A burner 15  
14    located in a lower portion of the steam generating boiler 17 introduces the powdered coal into the  
15    combustion chamber of the boiler and mixes it with the correct amount of additional air to burn the  
16    fuel efficiently. The boiler 17 is a large vessel which contains a tube assembly 19 in which water is  
17    heated and converted to steam, the steam then being used to drive the turbine 21. The boiler may  
18    also have associated NOx controls such as a selective catalytic reduction system (SCR) which reduces  
19    NOx emissions.

20

21    A coal combustion byproduct eventually falls to the bottom of the boiler combustion chamber where  
22    it is collected and discharged through duct 23. This bottom ash is used to make by product materials  
23    such as asphalt or concrete, or is disposed of in accordance with applicable law. A precipitator 25  
24    is used to capture particulate material and fly ash down stream of the boiler 17. The fly ash  
25    byproduct of the boiler combustion becomes entrained with and is carried out on the hot exhaust  
26    gases from the boiler 17. It is collected and has many uses similar to the bottom ash collected at 23.

27

28    A scrubber 27 is located downstream of the boiler and is used to remove SO<sub>2</sub> from the boiler exhaust  
29    gases (flue gases). The exhaust gases then pass to a stack 29 which is used to exhaust and disperse

1 the hot flue gases from the boiler. Emission monitoring equipment monitors the exhaust gases leaving  
2 the stack 29. The tower 28 is used to provide cooling water for the generator and to supply water  
3 to the boiler tube assembly 19. The primary conduits 30 communicate with a condenser 32 which  
4 converts the steam from the turbine back into water, which is recirculated through the secondary  
5 conduits 34 to the boiler, where it is again heated to form steam.

6

7 The generator 21 transforms the mechanical energy of the turbine into electric energy. A transformer  
8 31 increases the output voltage of the generator while reducing the current to make the transmission  
9 of electricity more efficient. The resulting electricity is fed to an electric utility represented by the  
10 towers 33.

11

12 The present invention concerns the discovery that, if a calcium hydroxide slurry, of controlled and  
13 specified physical and chemical characteristics, is injected into the SO<sub>3</sub> containing flue gas at a point  
14 in the exhaust gas duct where the temperature is sufficient to evaporate the water from the slurry but  
15 is low enough not to decompose the calcium hydroxide to calcium oxide, that such injection will  
16 result in the formation of solid calcium sulfate (as well as a mixture of calcium sulfite, calcium  
17 carbonate, calcium oxide and calcium hydroxide) which can be easily removed by particulate removal  
18 systems such as a bag houses or electrostatic precipitators (ESP).

19

20 The calcium hydroxide slurries which are used in the practice of the invention can be formed by either  
21 slaking quicklime or from lime hydrate. Calcium oxide (CaO) is often referred to as quicklime, while  
22 Ca(OH)<sub>2</sub> is referred to as hydrated lime--both being referred to as "lime". Quicklime is usually in the  
23 form of lumps or pebbles. Dry hydrated lime is usually a powder. Either dry CaO or Ca(OH)<sub>2</sub> can  
24 be mixed with water to form a "lime" slurry (referred to herein as a calcium hydroxide slurry). In the  
25 case of quicklime, the water reacts with the quicklime in an exothermic reaction to form hydrated  
26 lime. This is often referred to as slaking. During the slaking of quicklime, large amounts of heat are  
27 generated which can significantly raise the temperature of the slurry. The elevated temperatures  
28 involved can actually provide benefits for enhanced reaction rates and SOx removal.

29

1 Lime slurries can be made in batches or in a continuous process. If a particular user requires a large  
2 amount of lime slurry at a particular site, large capacity slaking and storage tanks can be permanently  
3 located on the site. These tanks can usually provide a sufficient supply of lime and lime slurry for  
4 most operations. In some cases, however, it is not practical to provide permanent slaking or storage  
5 tanks for forming lime slurries. In such cases, the limited use of lime may not justify the investment  
6 required for construction and maintaining large capacity processing tanks and equipment.

7

8 Portable equipment for forming lime slurries which can be moved from one location to another are  
9 described by *Teague et al.* (Pat. No. 4,329,090) and *Shields et al.* (Pat. No. 5,507,572) and, more  
10 recently, in *Scholl et al.* (Pat. No. 6,412,974), assigned to the assignee of the present invention.  
11 Figures 3 and 4 illustrate the Scholl device which can be used to provide the calcium hydroxide slurry  
12 needed to practice the invention. The apparatus 110 includes a unitary frame 111 that is substantially  
13 parallel to the ground, road, or highway when in use. Tank body 113 is attached to the frame 111,  
14 and has a horizontal axis 114 parallel to the horizontal axis 112 of the frame. The tank body has an  
15 exterior surface 201 and an interior surface 203 (Figure 4). The tank body forms at least one mixing  
16 chamber 205. The tank body is formed such that the temperature of the hydration reaction within can  
17 be controlled. The tank radiates heat generated by the reaction, and the rate of addition of the solid  
18 lime can further control the temperature. Thus, the walls of the tank body serve as one means of  
19 controlling the reaction temperature, the walls easily radiating the heat generated within the mixing  
20 chamber 205 to the external surroundings.

21

22 Within the mixing chamber 205 is the mixer 207 (Figure 4), the mixer in the present embodiment  
23 being an auger with a plurality of paddles 213 extending perpendicularly along the shaft 211. The  
24 mixer is driven by a hydraulic power unit (not shown) located on either the forward or rear platforms,  
25 the shaft 211 being driven to turn the paddles. The liquid and solid additives will fill the mixing  
26 chamber 205 to substantially cover the mixer. Once the mixing auger is activated it will sufficiently  
27 agitate the slurry, thus facilitating the hydration reaction and creating a more consistent mix of  
28 material.

1 Referring back to Figure 3, forward platform 115 is used to contain power unit 123. Power unit 123  
2 is a combustion engine, typically being a diesel engine. The combustion engine 123 serves to power  
3 all other devices on the apparatus indirectly; the combustion engine is coupled to the hydraulic power  
4 converter 119 that converts the torque of the combustion engine drive shaft into hydraulic power.  
5 This hydraulic power is then communicated through hydraulic lines to other hydraulic power units  
6 on the apparatus, such as, for example, hydraulic landing cylinder 129, suction pump 121, and a  
7 delivery pump (not shown). The suction pump 121 is used to draw slurry from the tank 113 to  
8 primary tube 139 and delivery outlet 127, while the delivery pump is used to draw solid lime from an  
9 external source into the tank 113 through inlets 125 and/or 125'.

10  
11 The tank body 113 can be one single compartment or can be divided into separate compartments.  
12 Generally, the tank body is one compartment. In a multi-compartment embodiment, one  
13 compartment can be for the initial reaction and mixing of the lime and water, and another  
14 compartment can be used to hold the reacted and ready to use slurry so that a continuous feed of  
15 slurry can be provided. The pump 121 in that case would pump slurry from the compartment holding  
16 slaked lime to the delivery outlet 127. Another pump would be provided to pump the slaked lime  
17 from the reaction compartment to the holding compartment.

18  
19 In order to expedite the delivery of the quicklime solid to the apparatus, at least two inlets 125 and  
20 125' are provided for each side of the apparatus 110. The inlets penetrate the tank body 113 at  
21 spaced apart vertical locations on the external cylindrical sidewall thereof. The spaced locations are  
22 above an imaginary midline (126 in Figure 3) drawn to intersect the cylindrical sidewall and divide  
23 the sidewall into quadrants. The horizontal spacing of the inlets is determined by the nature of the  
24 delivery means, i.e., the size of the delivery truck utilized, etc. Thus, a truck can pull alongside either  
25 side of the apparatus 110, and hoses can be attached to the inlets 125 and 125'. The inlets are  
26 arranged such that the quicklime is pumped below the surface of the water level inside the tank body  
27 113. This is accomplished by providing tank inlet extensions 209 and 209' (Figure 3), the extensions  
28 protruding from the inlets 125 and 125' down into the water within the tank. This improves the  
29 mixing of the solid and the water in the tank and prevents the lime dust from becoming airborne.

1 Once the quicklime is added to water inside the tank, the mixture is agitated using a mixing device  
2 such as auger 207. The augers are driven by a hydraulic motor attached to the platform 115 or 117.  
3

4 The reacted, hot slurry is then pumped by suction pump 121 from the tank body 113 to delivery  
5 outlet 127. The delivery outlet is shown in its assembled delivery position in Figure 3, and in a  
6 disassembled, traveling position in Figure 4. The delivery outlet is a rigid tube that is coupled to  
7 primary tube 139 through joint 131. Primary tube 139 is coupled to the pump 121 though joint 135.  
8 In use, the tank 113 is filled with water from a suitable water source. When the tank body 113 is  
9 filled with water, the quicklime or hydrated lime is then blown or otherwise introduced into the tank  
10 through inlet(s) 125 and/or 125' below the water level inside the tank through 209 and 209'.  
11 Simultaneous to this, the mixture is stirred by activation of the mixing device, or augers 207.  
12

13 The amount of lime solids added to the tank 113 may range between 20-45% by weight to that of the  
14 total lime slurry. For example, 158,000 lbs. of water may be used to fill the tank to a preselected  
15 level. To this may be added 50,000 lbs. of lime. The lime used may be either quicklime or hydrated  
16 lime. High calcium lime is usually preferable for most applications, although dolomitic lime can be  
17 used. The lime may have impurities but will ordinarily be better than 90% CaO or Ca(OH)<sub>2</sub>,  
18 depending on the type of lime used. The preferred solids content of the resulting slurry will range  
19 from about 15-35% by weight, based on the total weight of slurry.  
20

21 By whatever means the slurry is obtained, the lime slurry is then injected into the exhaust gas duct  
22 from the steam boiler at a point at which the exhaust gas duct temperature is within a desired range.  
23 Generally, the calcium hydroxide slurry will be injected into the duct where the temperature is below  
24 about 500-600EC.  
25

26 Figure 2 shows one point at which the lime slurry can be introduced into the exhaust gas duct. It will  
27 be understood by those skilled in the art that the example shown in Figure 2 is exemplary in nature  
28 only and is not intended to be limiting of the invention. In Figure 2, the flue gas passes from the  
29 boiler to an air heater 35 and from there to an electrostatic precipitator 37 before entering the

1 absorber 39 and being exhausted to the stack 41. The lime slurry 43 is pumped through dual nozzles  
2 into an injection point 44 upstream of the absorber 39. Compressed air from a source 45 is also  
3 introduced into the nozzles to produce a lime slurry droplet with a particle size in the range from  
4 about 40-50 micron. The atomized slurry is sprayed co-current with the off gas stream, dried and  
5 entered into the absorber. For the particular application illustrated, this operation was accomplished  
6 in less than one second retention time. A visible plume from the stack was eliminated. In some states  
7 "smoke watchers" are considered official and check for such visible plumes. The injection points 47,  
8 49 can also be utilized to inject lime slurry into the exhaust gas duct.

9

10 In some cases, where the power plant has a wet scrubbing system (such as scrubber 27 in Figure 1)  
11 which utilizes wet slaking of calcium oxide for the removal of oxides of sulfur in off gases, a portion  
12 of the wet slaked calcium oxide can be diverted from the wet scrubbing system and injected into the  
13 exhaust gas duct prior to the particulate removal system.

14

15 The use of calcium hydroxide slurry injection offers several non-obvious advantages. The gases in  
16 question are very soluble in water and this fact offers more contact with the dissolved calcium ion and  
17 solid calcium surface for enhanced removals and reagent utilization.

18

19 By controlling the viscosity and solids content of the calcium hydroxide slurry, also atomizing air if  
20 necessary, one can control the droplet size and the dispersability of the individual calcium hydroxide  
21 particles. By controlling the droplet size and dispersability of the calcium hydroxide, the ability to  
22 absorb and react with the small amount of SO<sub>3</sub> in the presence of larger amounts of SO<sub>2</sub> and CO<sub>2</sub> are  
23 greatly enhanced.

24

25 The evaporation of the water from the calcium hydroxide slurry after injection into the flue gas  
26 changes the micro environment surrounding the calcium hydroxide sorbent and thus has the ability  
27 to enhance the absorption and reaction process by providing a path way from SO<sub>3</sub> - H<sub>2</sub>SO<sub>4</sub> - CaSO<sub>4</sub>.  
28 The evaporation of the water from the injected calcium hydroxide slurry not only causes a higher

1 concentration of water vapor surrounding the calcium hydroxide sorbent particles, it also lowers the  
2 temperature surrounding the calcium hydroxide sorbent particles thus promoting SO<sub>3</sub> sorption.

3  
4 Since dry calcium hydroxide is a fine, white, low density powder it is almost always more expensive  
5 on an equivalent “Calcium” basis than calcium oxide, quicklime, and typically has higher delivery  
6 costs. As discussed above, calcium hydroxide slurry can be made from dry calcium hydroxide, or  
7 more importantly and less expensively directly from calcium oxide, quicklime. For facilities that  
8 would require only small amounts of calcium hydroxide for the removal of SO<sub>3</sub>, calcium hydroxide  
9 slurry can be purchased “as is” thus eliminating most of the capital and operating costs associated  
10 with a typical dry calcium hydroxide storage system.

11  
12 In current fossil fuel combustion systems that employ traditional wet lime scrubbing and are  
13 experiencing SO<sub>3</sub> problems, either because of installation of NOx control systems, such as SCR or  
14 because of other SO<sub>3</sub> concerns, this invention provides a simple and inexpensive method of capturing  
15 the SO<sub>3</sub>. Injection of the “on site” produced calcium hydroxide slurry will significantly reduce the  
16 concentration of SO<sub>3</sub> prior to the traditional wet scrubbing, thus eliminating the SO<sub>3</sub> plume “problem”  
17 without the installation of a dry calcium hydroxide injection system.

18  
19 In wet limestone scrubbing sulfur removal systems, the addition of a calcium hydroxide slurry duct  
20 injection system will remove the SO<sub>3</sub> prior to the post FGD wet limestone scrubbing, thus improving  
21 the overall efficiency of the combined sulfur removal processes. The use of residual lime from SO<sub>3</sub>  
22 removal provides enhanced overall SO<sub>2</sub>/SO<sub>3</sub> removal in such systems.

23  
24 Because calcium hydroxide has a solubility of approximately 0.2% in cold water, the use of a  
25 saturated calcium hydroxide solution can also be used to remove SO<sub>3</sub> when large amounts of water  
26 can be added to the flue gas without causing down stream problems. This saturated calcium  
27 hydroxide solution could yield improved SO<sub>3</sub> removal efficiency.

1 While the invention has been shown in only one of its forms, it is not thus limited but is susceptible  
2 to various changes and modifications without departing from the spirit thereof.  
3